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BALLOON PROFILES OF STRATOSPHERIC NO_2 AND HNO_3 FOR TESTING THE HETEROGENEOUS HYDROLYSIS OF N_2O_5 ON SULFATE AEROSOLS

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Abstract. Simultaneous in situ measurements of stratospheric NO_2, HNO_3, HCl, and CH_4 from 34 to 74 km were made in August 1992 from Palestine, Texas, using the balloon-borne laser In-Situ Sensor (BLISS) tunable diode laser spectrometer. Although the measurements of NO_2, HNO_3, and NO_2/HNO_3 agree well with gas phase model calculations near 34 km where SAGE II data show little sulfate aerosol, this is not true at the lower altitudes where SAGE II shows high aerosol loadings. At 24 km the BLISS NO_2 and HNO_3 measurements are 70% lower, and 50% higher, respectively, than the gas phase model predictions, with a measured NO_2/HNO_3 ratio 5 times smaller. When the heterogeneous hydrolysis of N_2O_5 and $ClONO_2$ on sulfate aerosol of surface area densities matching the SAGE II measurements is added to the model, good agreement with the BLISS measurements is found over the whole altitude range.

Introduction

The large increases in number density and surface area of stratospheric liquid sulfuric acid droplets [see, special issue of Geophysical Research Letters, volume 19, number 2, 1992] accompanying the June 1991 eruption of Mt. Pinatubo [McCormick et al., 1992] present a unique opportunity for study of heterogeneous chemistry and its sensitivity to an ever-diminishing aerosol loading, as the atmosphere returns to background conditions. Earlier attempts to attribute changes in atmospheric photochemistry to heterogeneous chemistry have been frustrated by three factors: the lower levels of sulfate aerosol associated with earlier volcanic eruptions on with background conditions typical of the pre-Pinatubo period; the measurement uncertainty of earlier instrumentation; and the lack of data relating measurements to tracer fields to normalize dynamical effects.

Models predict that the largest perturbations to stratospheric chemistry caused by heterogeneous reactions

are associated with changes in the $NO_x (= NO + NO_2)$ to HNO_3 balance. Two heterogeneous hydrolysis reactions are thought to be of significance; that of N_2O_5, [Cadle et al, 1975], with a reaction probability of 0.1 independent of temperature, and that of $ClONO_2$, with a reaction probability of only 0.0012, but increasing with decreasing temperature [see DeMore et al, 1992]:

$$N_2O_5 + H_2O \rightarrow 2HNO_3(g) \qquad (1)$$

$$ClONO_2 + H_2O \rightarrow HNO_3(g) + HOCl(g) (2)$$
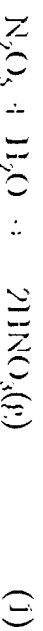
Over the temperature ranges of the mid-latitude lower stratosphere, the $ClONO_2$ reaction is expected to play a minor role in driving the conversion of NO_x to HNO_3.

The most direct method of establishing the occurrence of reaction (1) is to measure decreasing reactant, N_2O_5, and increasing reaction product, HNO_3, over an altitude range transitioning from little sulfate aerosol in the middle stratosphere to the heavy loading characteristic of the post-Pinatubo lower stratosphere.

Ironically, remote sensing satellite, shuttle, or balloon instruments with capability for simultaneous N_2O_5 and HNO_3 measurement do not perform well in the regions of high aerosol loading, where solar transmission at the synstracked wavelengths is greatly reduced. A re-analysis of ATMOS data by McElroy et al. [1992] has shown that while observed NO_2/HNO_3 ratios at 47°S below 30 km are better represented by a model incorporating heterogeneous chemistry, this same data set at 30°N is matched well by gas phase chemistry alone, although measured N_2O_5 is lower than the gas phase results.

The radicals NO_3 and NO are linked directly to the temporary reservoir N_2O_5, through the diurnal cycles of its nighttime formation and daytime photolysis, and are therefore considered good proxies of the temporary reservoir. Unlike N_2O_5, several reliable techniques exist for their atmospheric measurement, but the fast daytime photochemistry between them means that an isolated measurement of either gas is insufficient for testing heterogeneous chemistry without the simultaneous measurement of the other partner and of HNO_3.

The significant decreases in lower stratospheric NO and NO_2 after the eruption of El Chichon [McFarland et al, 1986; Roscoe et al, 1986] demonstrated the importance of heterogeneous chemistry, with models able to approximate the observed changes [Hofmann and Solomon, 1989; Michelangeli et al, 1989], but not the specific mechanism. More recent observations of NO_x abundances lower than gas phase predictions [Webster et al, 1990] did not include measurement of HNO_3.

Large differences between observed NO_2 and gas phase model predictions were reported following the eruption of Mt. Pinatubo. Johnson et al. [1992] reported a sudden drop by 35-45% in column NO_2 amounts over New Zealand. Observations of the NO_2 column over Colorado in spring 1992 [Mills et al., 1993] showed strong anti-correlation with increasing aerosol amount near 25-30 km, the effect saturating at higher aerosol loading.

Conclusive evidence of the occurence of reaction (1) came from simultaneous in-situ measurements of NO and NO_2 [Fahey et al., 1993]. Reductions in NO_x were observed for both background and volcanic aerosol conditions. Although this study was limited to altitudes ≤ 20 km, values of NO_x/NO_y as low as 5%, and 3 times smaller than gas phase values, were reported.

Balloon measurements of ClO profiles from 15 to 30 km from New Mexico (34 °N) by Avallone et al. [1993] and from Greenland (67°N) by Dessler et al. [1993] reported ClO amounts significantly greater than gas phase model predictions, and identified heterogeneous sulfate chemistry as the source of the increases.

In this paper, we report the first simultaneous in-situ measurements of NO_2 and HNO_3 since the eruption of Mt. Pinatubo over the altitude range 24-34 km from Palestine, Texas (32°N), and compare the data with the Caltech-JPL photochemical model incorporating heterogeneous chemistry constrained by simultaneous satellite measurements of aerosol loading, O_3, H_2O, temperature and pressure.

The BLISS Instrument

The Balloon-borne Laser In Situ Sensor (BLISS) instrument is a tunable diode laser infrared absorption spectrometer which over the last decade has made stratospheric measurements of numerous gases, including NO, NO_2, HNO_3, O_3, HCl, H_2O, CH_4, and N_2O [Webster et al., 1990, May and Webster, 1993]. Molecular number densities are measured directly using long-path absorption spectroscopy and harmonic detection techniques to sample a 200-300 m path between payload gondola and lowered retroreflector. For wavelength calibration, unambiguous identification of molecular species is ensured by the use of on-board reference cells of NO_2, HNO_3, HCl and CH_4 (see Figure 1, and May and Webster [1992]).

The Caltech-JPL Model

A simplified version of the Caltech-JPL 1-dimensional time-dependent photochemical model [Allen and Delitsky, 1991] was used, which included chemical kinetic rate

constants based of I the JPL compilation of DeMore et al.,
[1990], and photolysis rate coefficients with a full
treatment of the spherical geometry of the atmosphere.

The basic technique adopted was to constrain the
model using abundances of: NO_y estimated from the
BLISS HNO_3 and NO_2 measurements combined with
expected values for $ClONO$ and N_2O_5; Cl from the
BLISS HCl measurements and expected values of $ClONO_2$
and ClO; and O_3 and H_2O from the Microwave Limb
Sounder (MLS) [Waters et al., 1993] on the Upper
Atmospheric Research Satellite. The model ('1 was
initialized with all the NO_y entered as NO_2, and the initial
values of all the other NO_y species set to zero for
maintaining mass balance. This method has the advantage
of providing solutions to the coupled system of differential
equations unbiased by initial values, but to reach a steady
diurnal state the model has to be run for 11101(than 40
model days, mainly due to the long lifetime of HNO_3
below 30 km. A similar procedure was adopted for total
free chlorine by entering it exclusively as HCl. The ozone
concentration was kept fixed at the observed MLS values.

A first control run including gas-phase chemistry only,
was stopped at 4 am (time of" the BLISS measurement at
24 km). The resulting atmosphere was then taken as
initial conditions before adding the two heterogeneous
reactions (1) and (2). The products of both reactions
were assumed to be in the gas phase, as laboratory
experiments suggest [Reihs et al. 1990]. The adopted
aerosol profiles shown in Figure 2 are based on
Stratospheric Aerosols and Gas Experiment (SAGE II)
measurements in September 1990 and September 1992.
Aerosol surface area densities were retrieved from the
observed SAGE II extinctions by assuming a lognormal
size distribution for the background loading [Yue et al.,
1986]. Because the eruption of Mt. Pinatubo generated
relatively large particles in the stratosphere [Ansmann et
al., 1993], two lognormal size distributions describing the
bimodal behavior were required. In order to reach a
repeatable diurnal cycles in the cases of post-volcanic and
background conditions, additional model times of 3 days,
and 2 weeks, respectively, were needed, reflecting the
rapidity of the changes introduced by heterogeneous
chemistry on enhanced aerosol surface area. Despite the
limitations of using a 1-dimensional model, the validity of
this approach was supported by meteorological data
showing zonally-symmetric temperatures and weak winds
during August 1992 [G. Manney, private communication].

Results and discussion

Table 1 lists the BLISS measurements for the flight of

FIG. 2

August 26, 1992. Figure 3 compares the BLISS measurements of NO_2 and HNO_3 mixing ratios between 18 and 36 km with the model predictions. To construct the profile at 4:00 a.m. (solar zenith angle (SZA) of 127°) Inc. measured values at 32 and 34 km were adjusted slightly to correct for the nighttime conversion of NO_2 to N_2O_5 [Webster et al., 1990], based on a simple expression dependent on ozone concentration [Toumi et al., 1991]. Model runs are shown at the same SZA. Nitric acid has a much longer lifetime than NO_2, and does not exhibit diurnal variations, so the values for the measurements at 24, 26 and 34 km are used directly from Table 1, and compared with model predictions in Figure 3. Figure 4 Snows a plot of Inc. measured NO_2/HNO_3 ratio as a function of altitude, compared to model predictions.

Immediately apparent from Figures 3 and 4 is the general good agreement between observation and model results at the higher altitudes above 30 km, where aerosol Sill face area densities are negligible, and model calculations using both gas and heterogeneous chemistry converge. At the lower altitudes, however, as aerosol surface area density increases, the measurements depart markedly from the model calculations using only gas phase photochemistry. At 24 km the measurements of NO_2 and HNO_3 are 70% lower, and 50% higher, respectively, than the gas phase model predictions, with a measured NO_2/HNO_3 ratio 5 times smaller.

When the heterogeneous hydrolysis of N_2O_5 and $ClONO_2$ on sulfate aerosol of surface area densities matching the SAGE II measurements is added to the models, good agreement with the BLISS measurements of NO_2 and of HNO_3 is found over the whole altitude range. Note that vertical mixing, which the model does not account for, occurs on timescales of 1 to 3 months, compared with the interconversion between NO_x and HNO_3 which reaches steady-state after a little more than a month. This may explain why the model calculations have a tendency to overestimate the long-lived reservoir HNO_3. The contribution of uncertainty in the estimate of NO_y is minimized by considering the ratio of NO_2/HNO_3.

The dramatic differences in the ability of the gas phase and heterogeneous models to fit the data are seen in the comparison with the calculated NO_2/HNO_3 ratios (see Figure 4). Good agreement near 34 km is found with or without heterogeneous chemistry included (since aerosol surface area is small). At 24 km, however, a factor of 5 distinguishes the two cases, and the addition of heterogeneous chemistry is needed to match the low observations of NO_2/HNO_3. Background aerosol loading does not convert enough NO_2 to HNO_3 to account for the observed ratio. For both altitudes, the agreement between

[FIG. 3]

[FIG. 4]

heterogeneous model and measurement is remarkable. A measurement of NO_2/HNO_3 of 1 ."/ at 31 kill made close to 4:00 a.m. on an earlier BLISS flight in September 1988 is also shown in Figure 4, and agrees well With the model results.

The BLISS observations of NO_2 and HNO_3 14 months after the eruption of Mt. Pinatubo can be simulated only upon the inclusion of heterogeneous NO_y hydrolysis in model calculations. This result is particularly significant since purely gas-phase calculations initialized with ATMOS 1985 measurements reproduced the ATMOS data set well throughout the whole stratosphere. The observations are consistent with observations of low NO/NO_y ratios near 17-20 kill [Fahey et al., 1993].

References

Allen, h4., and M.L. Delitsky, Stratospheric NO, NO_2 and N_2O_5: a comparison of model results With Spacelab 3 Atmospheric Trace Molecule Spectroscopy (ATMOS) measurements, J. Geophys. Res., 95, 14077-14082, 1990.

Ansman, A.R., U. Wandinger, and C. Weitkamp, One year observations of Mount Pinatubo aerosol with advanced Raman lidar over Germany at S3.5 "N, Geophys. Res. Lett., 20, '/11''/14, 1993.

Avallone, L.M., D.W. Toohey, W.] 1.1 Brune, R.J. Salawitch, A,] L. Dessler, and J.G. Anderson. In situ measurements of ClO and ozone: implications for heterogeneous chemistry and mid-latitude ozone loss, submitted to Geophys. Res. Letters, 1993.

Cadle, R.D., 1', Crutzen, and D. Ehhalt, Heterogeneous Chemical Reactions in the Stratosphere, J. Geophys. Res., 80, 3381-3385, 1975.

DeMore, W.M., S.1'. Sander, C.J. Howard, A.R. Ravishankara, D.M. Golden, C.E. Kolb, R.F. Hampson, M.J. Kurylo, and M.J. Molina, Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation Number 10, JPL Publication 92-20, 1992.

Dessler, A.E., R.M. Stimpfle, B.C. Daube, R.J. Salawitch, E.M. Weinstock, D.M. Judah, J.D. Burley, J.W. Munger, S.C. Wofsy. J.G. Anderson, M.P. McCormick, and W.P. Chu, Balloon-borne measurements of ClO,

NO$_y$ and O$_3$ in a volcanic cloud: an analysis of heterogeneous chemistry between 20 and 30 km, submitted to Geophys. Res. Lett., 1993.

Fahey, D.W., S.R. Kawa, E.L. Woodbridge, P.Jin, J.C. Wilson, H.H. Jonsson, J.E. Dye, D. Baumgardner, S. Borrmann, D.W. Toohey, L.M. Avallone, M.H. Proffitt, J. Margitan, M. Loewenstein, J.R. Podolske, R.J. Salawitch, S.C. Wofsy, M.K.W. Ko, D.E. Anderson, M.R. Schoeberl, and K.R. Chan, In-situ measurements constraining the role of sulphate aerosols in mid-latitude ozone depletion, Nature, 363, 509-514, 1993.

Hofmann, D.J., and S. Solomon, Ozone destruction through heterogeneous chemistry following the eruption of El Chichon, J. Geophys. Res., 94, 5029-5041, 1989.

Johnston, P.V., R.L. McKenzie, J.G. Keys, and A.W. Matthews, Observations of depleted stratospheric NO$_2$ following the Pinatubo volcanic eruption, Geophys. Res. Lett., 19, 211-213, 1992.

7   ay, R.D., and C.R. Webster, In-situ Stratospheric Measurements of HNO$_3$ and HCl near 30 km using the BLISS Tunable Diode Laser Absorption Spectrometer, J. Geophys. Res., 94, 16,343-16,350, 1989.

7   ay, R.D., and C.R. Webster, Data processing and calibration for tunable diode laser harmonic absorption spectrometers, J. Quant. Spect. Rad.Transfer, 49, 335-347, 1993.

McCormick, M.P. and R.E. Veiga, SAGE II measurements of early Pinatubo aerosols, Geophys. Res. Lett., 19, 155-158, 1992.

McElroy, M.B., R.J. Salawitch, and K. Minschwaner, The Changing Stratosphere, Planet. Space Sci., 40, 373-401, 1992.

McFarland, M., B.A. Ridley, M.H. Proffitt, D.L. Albritton, T.L. Thompson, W.J. Harrop, R.H. Winkler, and A.L. Schmeltekopf, Simultaneous in-situ measurements of nitrogen dioxide, nitric oxide, and ozone between 20 and 31 km, J. Geophys. Res., 91, 5421-5437, 1986.

Michelangeli, D., M. Allen, and Y.L. Yung, The effect of El Chichon volcanic aerosols on the chemistry of the stratosphere through radiative coupling, J.Geophys. Res., 94, 18429-18443, 1989.

Mills, M.J., A.O. Langford, T.J. O'Leary, K. Arpag, H.L. Miller, M.H. Proffitt, R.W. Sanders, and S. Solomon, Geophys. Res. Lett., 20, 1187-1190, 1993.

Reihs, C.M., D.M. Golden and M.A. Tolbert, Nitric acid uptake by sulfuric acid solutions under stratospheric conditions: determination of Henry's law solubility, J. Geophys. Res., 95, 16545-16550, 1990.

Roscoe, H.K., R.J. Gray, R.J. Wells, and J.A. Pyle, Simultaneous measurements of stratospheric NO and NO$_2$ and their comparison with model

predictions, J. Geophys. Res., 91, 5405-5419, 1986.

Toumi, R., J.A. Pyle, C.R. Webster, and R.D. May, Theoretical interpretation of N_2O_5 measurements, Geophys. Res. Lett., 18, 12.13-1? 1/, 1991.

Waters, J.W., L. Froidevaux, W.G. Read, G.L. Manney, L.S. Elson, D.A. Flower, R.F. Jarnot, and R.S. Harwood, Stratospheric ClO and O₃ from the MLS 011 the UARS satellite, Nature, 362, 597-602, 1993.

Webster, C.R., R.D. May, R. Toumi, and J. Pyle, Active Nitrogen Partitioning and the Nighttime Formation of N_2O_5 in the Stratosphere: Simultaneous In-situ Measurements Of NO, NO_2, HNO_3, O_3, N_2O, and jNO_2 using the BLISS Diode Laser Spectrometer", J. Geophys. Res. 95, 13,8ss " 13,866, 1990.

Webster, C.R., R.D. May, D. Toohey, L.M. Avallone, J.G. Anderson, P.A. Newman, L.R. Lait, M.R. Schoeberl, J. Elkins, and K.R. Chan, Chlorine chemistry on polar stratospheric cloud particles in the Arctic winter, Science ?.61, 11301134, 1993.

World Meteorological Organization, Scientific Assessment of Ozone Depletion: 1991, WMO Rep. No. 25, Global Ozone Res. and Monit. Proj., Geneva, 1991.

Yue, G.K., M.P. McCormick, and W.)'. Chu, Retrieval of composition slid size distribution of stratospheric aerosols with the SAG] 11 satellite. experiment, J. Atm. Ocean. Technol., 3, 371-380, 1986.

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Webster et al.: Balloon NO_2 and HNO_3 profile.s

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Fig. 1. Second harmonic BLISS flight spectrum for NO_2 at '/.4 mbar compared with a synthetic spectrum.

Fig. 2. SAGE measurements of the total aerosol surface. area density profile at 30°N in Sept. 1992 (close. to the BLISS flight date) and in Sept. 1990 (background conditions prior to the eruption of Mt. Pinatubo).

Fig. 3. BLISS measurements of NO_2 and HNO_3 mixing ratio between 18 and 36 km compared with model predictions using gas-phase chemistry only (solid line), and including heterogeneous chemistry on background (dash-dot line) and volcanic (dashed line) aerosol.

Fig. 4. BLISS measurements of the NO_2/HNO_3 ratio between 18 and 36 km compared with model predictions using gas-phase chemistry ory (solid line), and including heterogeneous chemistry on background (dash-dot line) and volcanic (dashed line) aerosol. The data point representing NO_2/HNO_3 ' 1.74 at 31 km is from an earlier BLISS flight in 1988.

Table 1. BLISS data for balloon flight of August 26, 1992.

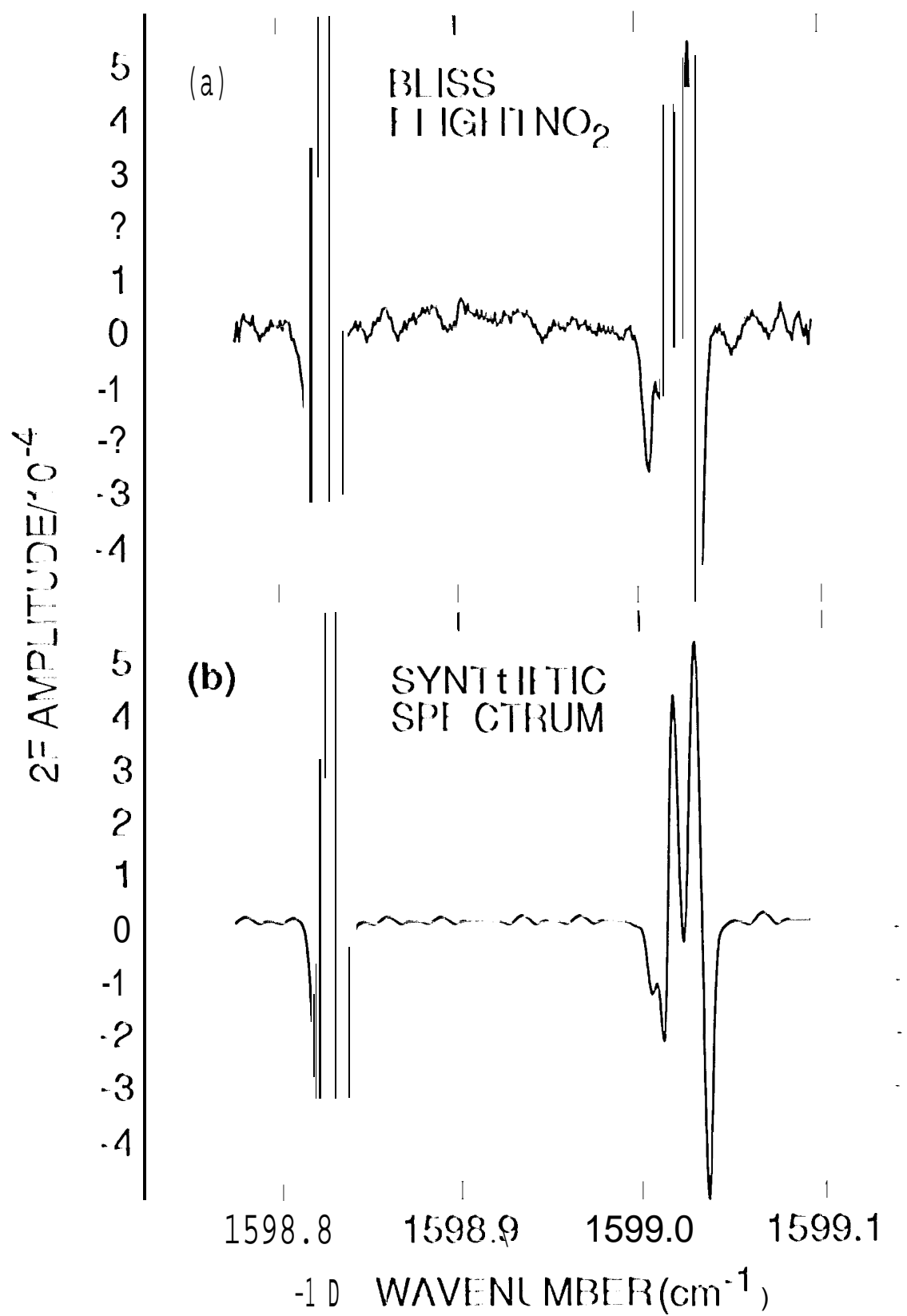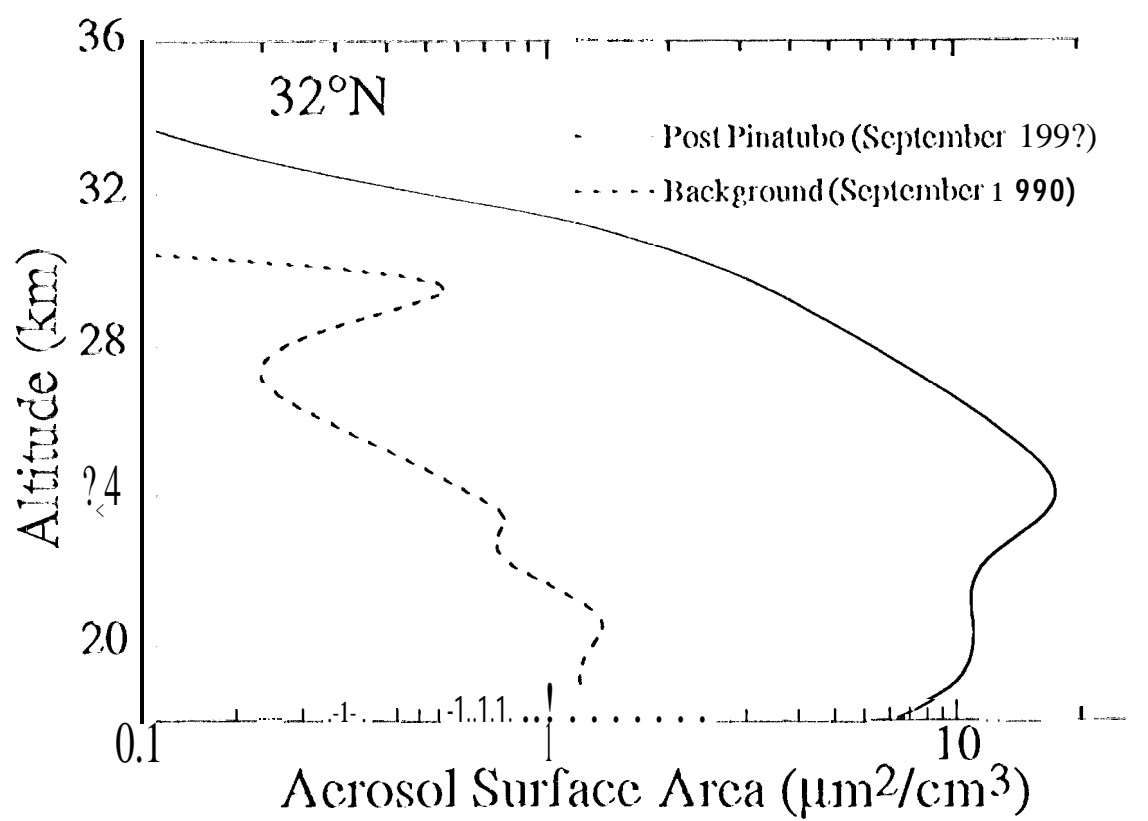| Gas	Local Time	Lat., Long.	Press. (mbar)	Temp. (K	Mixing Ratio (
NO$_2$	11:54 p.m.	31°47,97°32	7.4	231	6.8 ± 0.-/
	1:44 a.m.	31'35,s1[$°45	9.5	229	3.7 ± 0.7
	4:00 a.m.	31'3G,W'43	29.1	215	0.7 ± 0.2
HNO$_3$	12:48 a.m.	31°43,980 6	6.7	227	1.5 ± 0.5
	03:32 a.m.	31037,9s?039	27.7	216	6.1 ± 0.7
	05:18 a.m.	31039,100°5	29.1	213	7.1 ± 0.8
HCl	11:22 p.m.	31°49,97014	7.2	233	1.98 ± 0.20
	2:34 am.	31'3[1,99°11	18.1	219	1.34 ± 0.15
	3:06 a.m.	31°38,99°27	25.3	218	1.17 ± 0.12
	4:24 a.m.	3103&$19048	30.?	213	1.17 ± 0.1?
CH$_4$	12:28 p.m.	31°45,97°52	7.1	229	820 ± 40
	2:51 a.m.	31°38,99°21	21.2	216	1080 ± 50
	4:40 a.m.	31°38,99°53	31.0	223	1240 ± 60

FIGURE 1

FIGURE 2

FIGURE 3

Legend (within figure):
● 111.1ss 92
◆ BLISS 88
— · Gas phase only
---- · Background (1990)
----- Post Pinatubo (1992.) , ."-

Axes: Altitude (km) vs NO_2/HNO_3

FIGURE 4